In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

7/25/68

REMOVAL OF HEXAVALENT CHROMIUM COMPOUNDS FROM INDUSTRIAL WASTES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

Robert F. Weeks

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

Georgia Institute of Technology

December, 1971

REMOVAL OF HEXAVALENT CHROMIUM

COMPOUNDS FROM INDUSTRIAL WASTES

Approved:

Chairman

Date approved by Chairman: 11/22/71

ACKNOWLEDGMENTS

I would like to acknowledge the guidance and contributions of those who have assisted me in presenting this study. Dr. G. L. Bridger served as chairman of the Thesis Reading Committee. Without his guidance and experience this work would not have been possible. A great deal of appreciation is also extended to Dr. L. D. James and Dr. J. D. Muzzy for their advice and review of the thesis while serving on the Thesis Reading Committee.

I also wish to thank the Environmental Protection Agency - Office of Water Programs for their support under Training Grant 5P2-WP-226-02 and -03.

TABLE OF CONTENTS

Table of Contents (Continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The raw material for manufacturing chromium and chromium compounds is the mineral chromite. All of the chromite consumed in the United States is imported. The reserves of high grade chromite in the United States represent only a one and one-half month supply.

The important sources of pollution from chromium and chromium compounds are in the production of chromium chemicals and in the end-product uses of chemicals. Practically all of the chromium chemicals are hexavalent chromium compounds. The extent of pollution discharges from end-product uses in the metal finishing industry is estimated to be 2.9 million gallons of chromium bearing waste per day.

The effects of hexavalent chromium compounds on human beings, experimental animals, soils and plants and fish have been both beneficial and destructive. The effect depends on the intensity and duration of the exposure, and the relative solubility of the chromium compounds in aqueous biological fluids. Hexavalent chromium compounds are very toxic to the micro-organisms used in sewage treatment, and the discharge of chromium wastes into sewers causes municipal treatment plants to become inoperative.

Cost estimates for an existing chemical treatment process to remove the chromium ions from the waste stream are reported to be as follows:

1. A total installed cost of $46,000 for a system for treating 90,000 gallons per day containing two to three ppm of hexavalent

chromium ion.

2. A maintenance and operating cost of $3500 per year, and chemical cost of 47 cents per pound of chromium removed.

The objective of the experimental phase of this research was to improve the more promising existing chemical treatment process, namely the $NaHSO_3$ - NaOH process, so that the chromium could be re-used.

Two hexavalent chromium bearing waste solutions (one much more concentrated than the other) were obtained from a local plating shop where the solutions were used for deposition of chromate conversion coatings. The solutions were analyzed by a volumetric procedure and were found to contain 321 mg of chromium per liter and 55.5 gm of chromium per liter. The Cr(VI) in the waste solutions was reduced to Cr(III) with $NaHSO_3$ and this reaction is very fast at a solution pH of two. The treatment of the Cr(III) with sodium hydroxide at a solution pH of nine results in the formation of the amphoteric hydrous chromic oxide ($Cr_2O_3 \cdot x\ H_2O$) which settles within 30 minutes in the concentration range of 160-963 mg of chromium per liter. Generally the other metals in solution will precipitate as hydroxides. The sludge compactions were from 8.0 to 32.4 percent of the original sludge volume, and the chromium removals were practically 100 percent.

The solution was decanted and the hydrous chromic oxide sludge was dried and then roasted at 1060 ± 40°F for 30 minutes to remove all the water of hydration. The chromic oxide formed was leached with mineral acids and ammonia solutions to remove any other metal oxides or impurities that may be present.

After leaching, the purified chromic oxide was dried. The oxide

was analyzed by fusing a sample with sodium peroxide to convert the chromium into a soluble form, and then analyzing for the chromium with the volumetric method previously discussed. Based on the results of the laboratory work performed, a new treatment process was proposed that can quantitatively recover practically 100 percent of the chromium from industrial waste streams, and the purity of the recovered chromic oxide is approximately 90 percent. The proposed treatment is more expensive than the existing treatments because more processing steps are involved, but it is believed that the value of the recovered chromic oxide will more than off-set the extra costs. A finely ground chromic oxide of 98.5 percent purity would sell for 54 cents a pound.

CHAPTER I

SOURCES OF CHROMIUM

Introduction

Chromium has found extensive uses in metallurgy, refractories and chemicals. The common valances of chromium are zero, three, and six. Elemental chromium is used in metallurgy (zero valance), trivalent chromium is used in refractories, and chromium chemicals are mostly hexavalent chromium compounds. The source of chromium pollution in water is primarily from the industrial use of chromium chemicals, much of which is from discarded baths used by the meatl finishing industry. These baths often contain more than two and a half pounds (300,000 ppm) of hexavalent chromium per gallon of solution (1). The present drinking water standards are 0.050 ppm of hexavalent chromium (maximum). Oral ingestion of hexavalent chromium compounds may lead to intense irritation of the gastro intestinal tract resulting in severe pain, nausea, and hemorrhages. The raw material for manufacturing chromium and chromium chemicals is chromite, and the consumption of this ore in the United States was 1,402,538 short tons in 1970 (2). Approximately 65 percent of the ore was used in the metallurgical industry, 20 percent was used for refractories, and 15 percent was used in the manufacture of chromium chemicals.

Chromium Minerals

Elemental chromium does not occur in nature, but is one of the

rock-forming elements of the earth's crust which occurs as spinels, silicates, and complex salts. Chromite is the only commercially important source of chromium. Chromite's high density and resistance to weathering cause it to be deposited economically by sedimentation in nature. Chromite is a spinel (3) with a composition represented by the formula (Mg Fe) $(Cr,Al,Fe)_2O_4$. The principal chromium bearing minerals and the compositions of natural chromite ores are listed in Tables 4 and 5 in the Appendix.

Resources in the United States

All of the chrome ore consumed in the United states is imported. The United States buys most of its high grade ore from the U.S.S.R., Philippines, Turkey, Republic of South Africa, Southern Rhodesia, Pakistan, and Iran. The largest chromite deposit in the United States (approximately 75 percent of the total reserves) is located in the Stillwater complex of Montana, and a lesser deposit (approximately 10 percent of the reserves) is located in Southern Oregon. The domestic reserves of chromite are estimated to be 2,000,000 long tons. Only 130,000 long tons would be recoverable as high grade ore (3). In terms of the 1970 consumption (2), the reserves of high grade ore represent less than a one and a half months supply. Canada is also essentially a non-producer of chrome ore with very shallow reserves. This makes chromium reserves strategic in North America.

Objective of Thesis

The objectives of this research were to make literature surveys on the types of sources of water pollution by chromium and chromium

compounds, the environmental effects of this pollution, and the state-of-the-art for chemical treatment of chromium bearing waste streams. A further objective was to test proposals for modifying an existing chemical treatment process in order to re-use the chromium compounds. A still further objective was to determine the economic feasibility of such a process.

CHAPTER II

SOURCES OF POLLUTION

Pollution from the Chemical Industry

Approximately 85 percent of the chrome ore is used for the production of metallurgical and refractory materials without any significant pollution being produced because these chromium products are in the elemental and trivalent state (4). The source of pollution is from industrial wastes from the manufacture of chromium chemicals and from the use of the chemical compounds. The chemical industry consumed 213,195 short tons of chromite in 1970 (2). Transvaal Grade B friable chromite (44% Cr_2O_3) is the only important ore for the production of chromium chemicals. Compositions of this ore are listed in Table 6 of the Appendix. Sodium chromate and sodium dichromate (both hexavalent chromium compounds) comprise over 75 percent of the production of chromium chemicals (3). A process flowsheet for the manufacture of sodium dichromate is shown in Figure 4 of the Appendix. The effluent water and particulate from these chemical plants constitute a major potential pollution source for hexavalent chromium, but data on the extent of pollution was not found in the literature. Commercial uses of the common chromium chemicals are listed in Table 7 of the Appendix.

Pollution from the Metal Finishing Industry

Dichromate compounds and chromic acid are extensively used in the metal finishing industry. A second major source of pollution comes from

discarded baths and the associated rinse waters. The chromium containing baths are used for the cleaning, pickling, etching, and polishing of metals and also for coating metals. The coatings are applied by electroplating, chemical conversion, and anodizing. There are between 15,000 and 20,000 metal finishing shops in the United States, and the volume of chromium bearing waste is estimated to be 2.9 million gallons per day (5). The reported concentration of this waste varied from one to seven hundred ppm of chromium ion. Chromium bearing wastes from the metal finishing industry are listed in Table 8 in the Appendix.

Pollution from Corrison Inhibitors

Because of their corrosion inhibiting properties, when present in only trace amounts, hexavalent chromium compounds play an important and unique role in corrosion prevention. Chromates are very effective for inhibiting corrosion in iron, lead, copper, zinc, and other metals. Practical applications include corrosion control in cooling towers, air conditioning, boilers, condensers, refrigerating brines and automobile radiators. The "blow-down" and flushing of this equipment is a source of pollution (6,7), but data on the quantity of pollutants was not found in the literature.

Pollution from Other Sources

Other potential sources of pollution include the use of chromium chemicals for paint pigments, mordants in the textile industry, chrome tanning of animal hides (8), fungicidal applications for wood preservatives, in matches and fireworks, welding rods, abrasives, and polishing compounds and as catalysts for petrochemical manufacture.

CHAPTER III

ENVIRONMENTAL EFFECTS

Effects on Human Beings

Metallic chromium and chrome ore (chromite) are considered to be practically inert in the human body and no harmful effects have been reported. Anionic hexavalent chromium ($CrO_4^{=}$) remains soluble at the body pH, but most forms of the cationic trivalent chromium are relatively insoluble at the body pH. Trivalent chromium is sometimes classified as a trace element essential to the normal function of carbohydrate metabolism. It has been clearly established that trivalent chromium supplementation of 150 to 1000 micrograms per day improved several cases of impaired glucose tolerance (9). However, hexavalent chromium compounds are corrosive, extremely irritative, and often toxic. In common with the other derivatives of heavy metals, the hexavalent chromium compounds may cause precipitation of tissue proteins.

The most common effects of chromium compounds on industrial workers result from the direct contact of the skin with hexavalent chromium compounds. The skin reactions consist of chrome ulcers, chrome dermatitus, and allergic dermatitus. The allergic dermatitus is caused by the development of a hypersensitivity to chromium compounds subsequent to "excessive" exposures (3). Although "chrome ulcers" are usually less than 1/8 inch in diameter, they are difficult to treat and; if not treated immediately with the proper medication (10), may penetrate the bone and become very painful. The chrome dermatitus appears as

extensive inflamatory papular eruptions on the skin and is caused by the irritating nature of hexavalent chromium compounds. The papular eruptions usually occur on the skin of the hands and forearms, but these eruptions may also occur on the skin of the ankles, feet, face, and back. Allergic dermatitus is caused by an allergic reaction to hexavalent chromium compounds. Dermatitus is less common than chrome ulcers. When a preparation of chrome was accidently substituted for sulphur in an antiscabetic ointment, 12 people were killed subsequent to external use. Concentrations of chromium in normal body tissues and in body tissues of chromate workers are shown in Table 9 in the Appendix.

The prolonged inhalation of hexavalent chromium compounds is reported to cause ulceration of the nasal septum, lung cancer, emphysema, chronic bronchitis, bronchopneumonia and other respiratory ailments. The most common effect from breathing dust or mist containing hexavalent chromium is the ulceration and perforation of the nasal septum. The incidence of perforation of the nasal septum was reported to be between 50 and 75 percent among chromate-workers in 1952 (3). Usually the perforations appears between the sixth and twelfth month of exposure. It is not painful, is limited to the cartilage part of the nose and does not interfere with normal breathing. The carcinogenic properties of chromium compounds is evidenced by the high incidence of cancer in the respiratory tract of chromate workers. Records of the Public Health Service in 1949 and 1950 showed that the incidence of lung cancer among chromate workers was ten times as great as in the other industries surveyed (3).

Effects on Animals

Experimental animals have been exposed to chromium compounds by inhalation and implanatation (11, 12). The results of experimental studies of the toxicity of chromium compounds with rabbits, guinea pigs, rats, mice and other animals are shown in Tables 10 and 11 in the Appendix. The inert nature of chromic oxide has led to its extensive use in studies of animal nutrition and metabolism (3).

Effects on Fish

Young Rainbow Trout and Chinook Salmon were exposed to varying concentrations of sodium dichromate for periods up to seven months. At hexavalent chromium concentrations of 0.020 ppm an inhibition growth was observed and at 0.080 ppm an increase in mortality was noted (13). Concentrations of two ppm of trivalent chromium have been reported as toxic to fish (14, 15). Two reported fish kills totalling 7,114 fish (16, 17) were associated with industries using chromium compounds. The toxicity of chromium ions to fish are listed in Table 12 in the Appendix.

Effects on Plants and Soils

Very little information is available to determine the specific effects of chromium concentration in the soil on plant growth. The type of soil, pH of the soil and solubility of the chromium compound present in the soil seem to be more important than the chromium concentration. It has been reported that soil concentrations of 0.01 percent chromium caused stimulation of growth with barley, but concentrations of 0.005 percent chromium were toxic to wheat. These chromium concentrations were available in the hexavalent form as chromates and bichromates (3).

Effects on Sewage Treatment

Chromium ions are extremely toxic to many of the microorganisms used in municipal sewage treatment (5, 8). Tests conducted with Escherichia Coli and Sachranycetes Ellipsoides bacteria showed that chromium ions drastically reduced their ability to reproduce (18, 19). The discharge of chromium wastes into sewers often causes destruction of trickling filter slimes and activated sludge processes. Concentrations of seven ppm of hexavalent chromium have caused (20, 21) treatment plants to be inoperative.

Effects on Materials

All hexavalent chromium compounds, in the form of chromic acid, chromates, or dichromates, are strong oxidizing agents, and chromic acid is also a strong acid. Chromic acid mists from plating shops have been reported to discolor paint finishes on automobiles and buildings. Chromic acid is also very corrosive to common metals.

CHAPTER IV

EXISTING TREATMENTS FOR CR(VI) WASTES

General

Processes for removal of hexavalent chromium ions from industrial waste streams include: electrolysis, dialysis, ion exchange, chemical treatment, and others. Electrolysis has the advantage of requiring the least amount of space (22). Good results were reported with dialysis when the chromic acid concentrations exceeded one pound per gallon of solution (23). Ion exchange resins have been used for removal of hexavalent chromium (24, 25). This process is usually followed by evaporation if the recovered metal solution is to be re-used. Hexavalent chromium has been removed by direct precipitation with barium compounds (26), but the most common method of removal is the reduction of hexavalent chromium to trivalent chromium with sulfur dioxide, and the precipitation of trivalent chromium with alkali (27, 28).

Ion Exchange

Use of ion exchange in waste treatment includes removal of impurities from hexavalent chromium baths with cation exchange resins so that the bath does not need to be discarded, removal of all impurities from waste streams utilizing both anion and cation resins and for the removal of hexavalent chromium (chromate ion) from waste waters with anion exchange resins. The anion exchange resins are usually regenerated with caustic solution and the hexavalent chromium regenerate concentration

is five to ten percent. The regenerate is evaporated if the chromium is to be re-used.

Cation exchange resins for purifying chromic acid anodize baths are usually very efficient. It has been reported that 99.8 percent of the aluminum, 99.5 percent of the iron and 94.8 percent of the trivalent chromium was removed from the chromic acid anodize baths at the Rock Island Arsenal (25). Theoretically, the continuous purification of these baths should virtually eliminate a source of pollution. The cation resins are regenerated with sulfuric acid, and the effluent is usually neutralized and discarded.

Anion resin and cation resin combinations remove practically all the ionic impurities so that the water may be re-used. The hexavalent chromium regenerate from the anion resins may be re-used, or regenerates from both resins may be easily disposed because of their concentration.

Chemical Treatment

Hexavalent chromium compounds may be directly precipitated by lead, silver and barium compounds. The Electrolux Corporation used barium sulfide (BaS) treatment in two - 20,000 gallon reaction tanks in 1939 (26). Although this treatment was effective for eliminating chromates from the waste stream, the process was discontinued in favor of sulfur dioxide salts and alkali, because the barium sulfide was difficult to dissolve, and hydrogen sulfide was formed in the processing. Some advantages of this process are the ease of handling and dewatering the sludge. The sludge volume is only approximately one half the volume of an equivalent amount of chromic hydroxide (hydrous chromium oxide), and the precipitated barium chromate has some value as a paint pigment.

Barium carbonate (witherite) has been used as both a neutralizing and precipitation agent for barium chromate (29). The barium carbonate goes into solution and the barium chromate precipitates out (30), because it is less soluble (0.34 ppm) than the carbonate compound (2.2 ppm). Barium chloride has also been used for precipitation of insoluble barium chromate. The disadvantage of this method is that barium chloride is very toxic, and therefore; the additions must be carefully controlled.

Since hexavalent chromium ions cannot be removed as the corresponding hydroxide by precipitation with alkali, these wastes require special treatment. The hexavalent chromium is first reduced to trivalent chromium with reducing agents such as sulfur dioxide, sodium salts of sulfur dioxide, ferric sulfate, scrap iron, or brass. The trivalent chromium is then precipitated as a hydrous oxide with alkali such as caustic, soda ash or lime.

The most commonly used reducing agent is sulfur dioxide. Sulfur dioxide is usually purchased in 150 pound cylinders as liquid sulfur dioxide, as a single valve and flow meter are sufficient to control the reaction. Sulfur dioxide requires less acid to control the waste solution pH, since sulfur dioxide readily combines with water to form sulfurous acid, the pH of the waste solutions should approach the original value as the sulfurous acid and hexavalent chromium are consumed in the reaction. The reaction kinetics, ionization constants and stoichiometry of these reactions are listed in Tables 13, 14, and 15 in the Appendix. Sulfur dioxide also combines with the dissolved oxygen in the solution to form sulfates and reduces other metals such as copper and manganese.

Alkali additions are made to the trivalent chromium solution until the solution pH is 8.5 to 9.0, (this is the minimum solubility of hydrous chromic oxide). Chromic hydroxide (hydrous chromic oxide) is amphoteric and is fairly soluble at or below a pH of eight and also at or above a pH of ten. After alkali additions, the metal precipitates are allowed to settle for approximately one and a half hours. The clear liquid is usually decanted and disposed through the sewer, and the hydrous metal oxide sludges are pumped to a lagoon or hauled to a dumping site.

CHAPTER V

EXPERIMENTAL WORK ON CHROMIUM WASTE TREATMENT

Sources of Test Solutions

Two chromium bearing waste solutions were obtained from a local plating shop. The solutions were used as chromate conversion coatings. These coating processes are proprietary, but the chromate conversion coating solution is always an acidic solution containing hexavalent chromium compounds, such as chromium trioxide, and small amounts of other compounds that function as catalysts. As these baths become depleted some of the hexavalent chromium is reduced to trivalent chromium, and the solution also becomes heavily contaminated with the basis metal ions such as Cu^{+2}, Zn^{+2}, Al^{+3}, Cd^{+2}, Fe^{+2}, or Fe^{+3}.

Analysis of Test Solutions

The test solution concentrations of total chromium, hexavalent chromium and trivalent chromium were determined by a volumetric quantitative analysis based on the valence change from six to three when the hexavalent chromium reacts with potassium iodide to form iodine. When analyzing for total chromium, the solution is purified by oxidizing all of the chromium compounds to Cr(VI) with peroxide and removing the other metal ions as the corresponding hydroxide by precipitation with NaOH (the Cr(VI) compounds cannot be removed as the corresponding hydroxide by precipitation with alkali). The solution is then treated with potassium iodide and the iodine liberated is titrated with sodium thiosulfate using

a starch indicator.

The Cr(VI) is determined by removing the Cr(III) and other metal ions as the corresponding hydroxides with NaOH then titrating with sodium thiosulfate to the starch-iodine end point previously mentioned. The difference between the total chromium concentration and the Cr(VI) concentration is the Cr(III) ion concentration.

Six samples of each solution were analyzed and one solution contained 55.5 grams of chromium per liter of solution and 93.4 percent was available as Cr(VI). The other solution contained 321 milligram of chromium per liter of solution and 82.9 percent was available as Cr(III). The results of these analysis are shown in Table 1.

Precipitation of Hydrous Chromic Oxide

The kinetics of the reaction of $NaHSO_3$ and Cr(VI) is favored by a pH less than or equal to two. These reaction rates are shown in Table 13. Sulfuric acid was used to adjust the solution pH to two and an excess of 1.412 lb. of sulfuric acid per lb. of Cr(VI) was added to the solution to maintain the solution pH at or less than two throughout the reaction according to the following equation (31):

$$3\ NaHSO_3 + 1.5\ H_2SO_4 + 2\ H_2CrO_4 = Cr_2(SO_4)_3 + 1.5\ Na_2SO_4$$

Theoretically only three pounds of $NaHSO_3$ is required to reduce one pound of Cr(VI), but the bisulfite is also consumed by the dissolved oxygen in the solution and by some of the other metal ions present. After 10 minutes of reaction time, the Cr(VI) should be completely converted to Cr(III). The Cr(III) solution was neutralized with NaOH until the solution pH was approximately nine. A more compact precipitate forms at a

Table 1. Analysis of Test Solutions

Solution Number	Sample Number	Total Cr (Mg/L) x 10^{-3}	Cr(VI) (Mg/L) x 10^{-3}	Cr(III) (Mg/L) x 10^{-3}
I	1	55.5	50.3	5.2
	2	57.2	51.1	6.1
	3	53.7	52.9	0.8
	4	55.5	52.0	3.5
	5	56.4	52.9	3.5
	6	54.6	51.1	3.5
	Average	55.5	51.8	3.7
II	1	0.330	0.0433	0.287
	2	0.295	0.0433	0.252
	3	0.338	0.0520	0.286
	4	0.330	0.0693	0.261
	5	0.330	0.0607	0.269
	6	0.303	0.0607	0.243
	Average	0.321	0.0549	0.266

Note: 1. The analytical procedures for determining total Cr & Cr(VI) are on pages 41 and 42

2. Sample calculations are shown on page 44

solution pH of nine, and this is also the pH at which hydrous chromic oxide has its minimum solubility. The solution pH should be controlled between eight and ten, because at a solution pH greater than ten or less than eight hydrous chromic oxide is very soluble.

Settling and Compaction Tests

Four test solutions with concentrations of 160,321,463 and 902 milligrams of chromium per liter were reduced with sodium bisulfite and precipitated with sodium hydroxide as hydrous chromic oxide. These four concentrations were chosen because the reported concentrations in waste streams were all less than 1000 ppm. The hydrous chromic oxide solution was transferred into a 250 ml. graduate cylinder and the settling and compaction were observed. The settling occurred quite rapidly and was practically complete in 30 minutes. The compaction after two hours of settling varied from 8.0 percent for the 160 mg/l concentration to 32.4 percent of the sludge volume for a concentration of 902 mg/l. Curves of settling and compaction rates are shown in Figures 1 and 2. The data for the settling and compaction tests are shown in Table 2.

Recovery of Chromic Oxide

The effluent from the hydrous chromic oxide solution was decanted, and the sludge was dried and roasted at 1060 $\pm$ 40°F. to remove all the water of hydration from the chromic oxide. The purity of the chromic oxide was 41.3 percent at this point.

Chromic oxide was reported to be insoluble in water, acetone, and alcohol and only slightly soluble in all acids and alkalies except 70 percent perchloric acid. The more soluble metal oxides such as Fe, Mn,

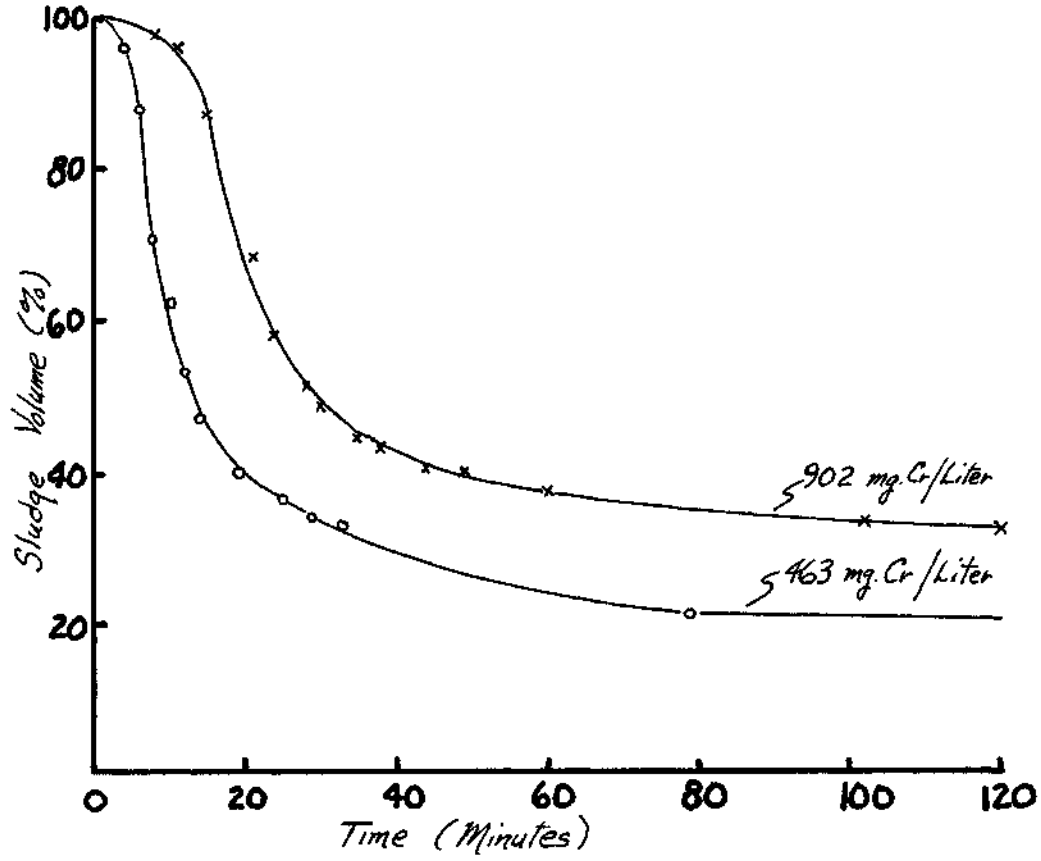

Figure I. Settling And Compaction Tests For Waste Solution No. I

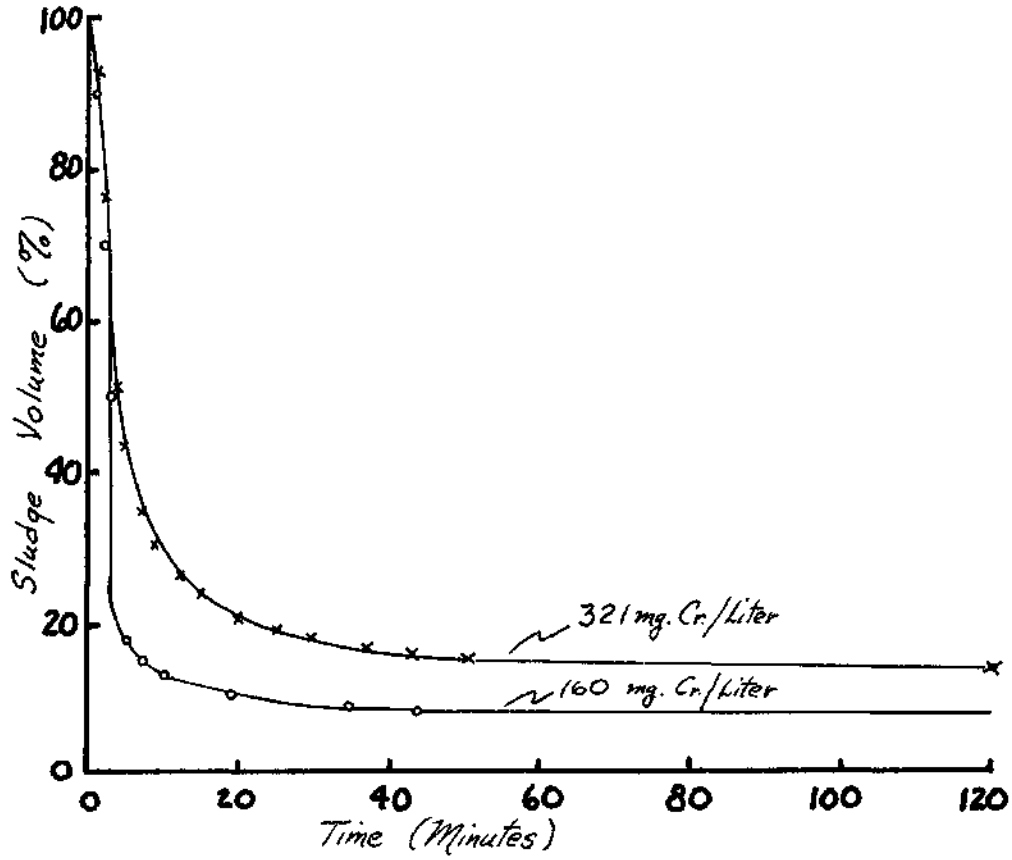

Figure 2. Settling And Compaction Tests For Waste Solution No. II

Table 2. Settling and Compaction Rates for Hydrous Chromic Oxide

160 (mg/l)		321 (mg/l)		463 (mg/l)		902 (mg/l)	
Time (Min)	Volume %	Time (Min)	Volume %	Time (Min)	Volume %	Time (Min)	Volume %
0	100	0	100	0	100	0	100
1	90	1	92.8	2.5	98	2	99.2
1.5	80	2	76.8	4	96	8	98
2	70	3	63.6	6	88	11	96
3	50	4	50.8	8.5	70.8	15	87.2
4.5	20	5	43.2	10	62.4	20.5	68.4
5	18	6	38.4	12	53.2	22	63.6
6	16.6	7	34.8	14	47.2	24	58.4
7	15.2	9	30.4	19	40	26	54.4
8	14.6	10	29.2	20.5	38.4	28	51.2
9	13.6	12	26.4	22.5	36.8	30	48.8
10	13.2	15	24.0	29	34.0	35	44.8
19	10.2	17.5	22.0	33	32.8	38	43.2
34.5	8.8	20	20.8	79	21.6	44	40.8
43.5	8.4	23.5	19.6	134	21.6	49	40
200	7.2	25	19.2			60	37.6
		30	18.0			102	33.6
		37	16.8			120	32.4
		43	16.0			129	32
		50.5	15.2				
		120	14.4				

Cd or Zn can be dissolved from the more inert chromic oxide with mineral acids or ammonia solution by an extraction of solids or leaching. The purified chromic oxide was dried, and the purity of the oxide approached 90 percent. The process flowsheet for recovery of chromic oxide is shown in Figure 3. Samples of the purified chromic oxide were fused with sodium peroxide, dissolved in deionized water, and analyzed for Cr(VI) in accordance with the procedure shown in the Appendix. The purity of the oxides are shown in Table 3.

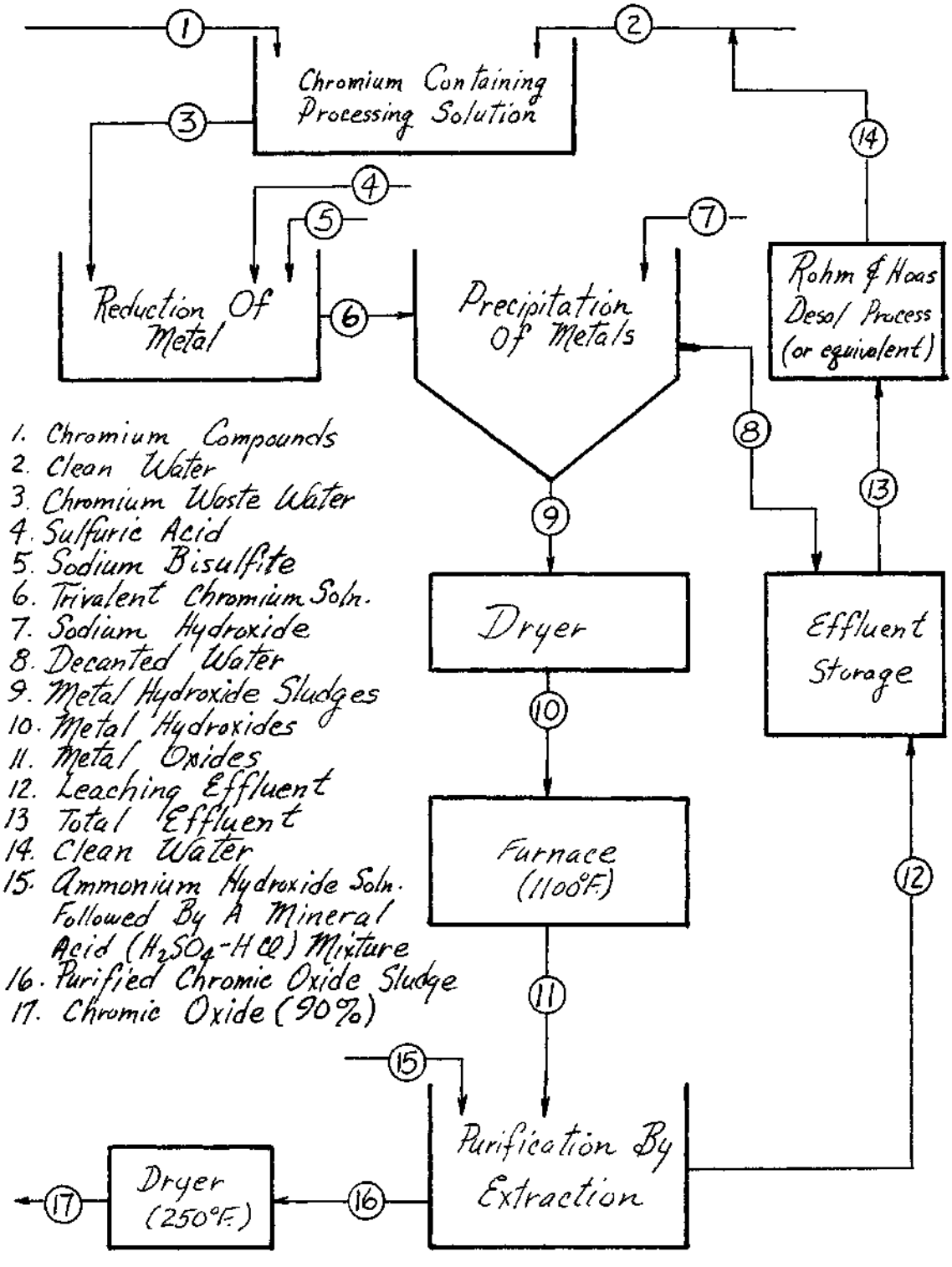

Figure 3. Flow Sheet For Recovery Of 90% Chromic Oxide

Table 3. Chromic Oxide Purity

Process	Sample Size (MG)	Titer (ML) 0.1N $Na_2S_2O_3$	Percent Cr_2O_3
Roasting	147.4	24.05	41.3
Leaching*	105.1	37.00	89.2
Leaching*	97.1	34.40	89.7

*These samples were filtered with Whatman No. 40 Filter Paper before roasting.

Leaching was performed with
1) 10 volume percent ammonium hydroxide (150°F)
2) deionized water (70°F)
3) 10 volume percent hydrochloric and sulfuric acids
4) deionized water

CHAPTER VI

ECONOMICS

Treatment of chromium bearing waste streams to prevent pollution of the receiving waters by removing the chromium are necessary for compliance with present water quality regulations. Cost estimates for an existing chemical treatment process are reported (6) to be as follows:

1. A total installed cost of $46,000 for a system for treating 90,000 gallons per day.
2. A maintenance and operating cost of $3,500 per year.
3. An average chemical cost of 47 cents per pound of chromium removed.

Cost items one and two probably do not vary much over ranges of concentration of hexavalent chromium ion up to 1000 ppm. The installed cost can be converted to an annual cost by use of the annual-cost method of discounting (31). Based on a minimum attractive rate of return of 15 percent and an equipment life of 15 years (32), the installed cost amounts to $7860 on an annual basis. At a concentration of 250 ppm of hexavalent chromium ion, the three costs sum to 64 cents per pound of chromium removed.

The effluent water from the liquid-sludge separation in the existing chemical treatments contains dissolved solids and has a high oxygen demand. Because water quality regulations are becoming more stringent, further treatment of this effluent water will probably be required in the future.

This effluent water could possibly be re-used, and the cost of purifying this water would be approximately 30 cents per 1000 gallon per 1000 ppm of waste ions up to a maximum of 3000 ppm of total dissolved solids (33).

There is a need for reclaiming chromium and other metals from the hydrous oxide sludges that are generated in waste treatment and presently discarded. These discarded sludges have a detrimental environmental impact in that they are soluble at a pH below eight or above ten and may be taken up in the ecosystem.

The recovery of the chromium from the hydrous oxide sludges in the experimental testing done in this study was practically 100 percent, and the purity of the chromic oxide approached 90 percent. The chromic oxide could be re-used for the manufacture of chromium chemicals. The average price for chromite of 40 percent or less in purity is $60 per long ton of chromic oxide content (2). If the chromic oxide purity could be raised to 98.5 percent (commercial grade), a finely ground chromic oxide could sell for 54 cents a pound (34, 35).

The proposed process for recovering chromium adds to the cost of the existing treatment processes for removing chromium from the water and discarding the wastes because it contains more steps, but it is believed that the savings in sludge disposal cost and the value of the recovery will more than off-set the extra costs. The proposed process has other advantages such as:

1. It is applicable to all sources of hexavalent chromium pollution mentioned in Chapter 2.
2. Waste treatment operators familiar with the existing chemical

treatment of chromium wastes should not need additional training to operate the new process.

3. The proposed process will comply with the present legal requirements for waste treatment and would also technically comply with the proposals for waste re-use in the future.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. By chemical reduction and precipitation, decanting drying, roasting, leaching, and redrying chromium can be quantitatively recovered from waste streams and purified to 90 percent in the form of Cr_2O_3.

Recommendations

1. Tests should be continued to further purify the recovered chromic oxide to increase its value.

2. Pilot plant studies should be conducted to evaluate further the economic feasibility of the proposed new process.

APPENDIX

Table 4. Chromium Minerals and Principal Chromium-Bearing Minerals (3)

Minerals	Cr_2O_3 (%)
Beidellite (volchonskoite)	Variable, up to 5
Chromite	15-65
Copiapite (knoxvillite)	7.4
Crocoite	21.9
Daubreelite	53.0
Dietzeite	13.9
Fornacite	No analysis
Halotrichite (redingtonite)	7.5
Kaemmererite	Variable, up to 12
Lopezite	35.4
Merumite	81.3
Muscovite (fuchsite)	Variable, up to 5
Phoenicochroite	31.2
Stichtite	22.3
Uvaravite	27
Vauquelinite	25.2

Table 5. Composition Variations of Chromites (3)

Compound	Composition Range
Cr_2O_3 (%)	16.41-62.75
Al_2O_3 (%)	0.76-51.32
Fe_2O_3 (%)	0 -50.28
FeO (%)	10.36-34.90
MgO (%)	0.25-17.72
Other (%)	0 - 6.50
Cr:Fe ratio	0.18- 4.34
Specific Gravity	3.891-4.53

Table 6. Typical Analysis of Chromite Used for Manufacturing Chemicals (3)

Compound	Percent
Cr_2O_3	44.3
Total iron as Fe	19.2
SiO_2	3.5
Al_2O_3	14.2
MgO	10.1
CaO	0.4
Vanadium as V	0.2

Table 7. Uses of Common Chromium Chemicals (3)

Compound	Commercial Use
Chromic Oxide (Cr_2O_3, mp = 4415°F.)	Refractory materials, abrasives, catalyst for chemical reactions, colorant for Portland cement, ceramic tile glazes, alkali-proof paints, concrete and bridge paints.
Chromium Trioxide (CrO_3)	Aluminum anodizing, chromium plating, as a corrosion inhibitor, etching and stripping aluminum, copper and zinc, de-oxidizing and for electro-polishing.
Sodium Dichromate ($Na_2Cr_2O_7$)	Corrosion inhibitor, deoxidizing, etching and stripping metals, mordants and tanning.
Sodium Chromate (Na_2CrO_4)	Primarily as a corrosion inhibitor and as an intermediary in chemical manufacture.

Table 8. Chromium-Bearing Wastes From Typical Plating Operations (5)

Type of Work Plated	Chromium-Bearing Waste			
	Volume, gal.	Analyses, ppm[a]		
		Cr	Ni	Cu
Aircraft engines and parts	440,630/day	--	--	--
Automobile bumpers	480,000/day	--	--	--
Automobile grills	100,000/day	700	--	--
Missile parts	80,000/day	1	--	--
Office furniture	24,000/day	--	--	--
Typewriters and office machines	50,000/day	16	39	--
Instrumentaion and control equipment	--	--	--	--
Electronic hardware	828,000/day	--	--	--
Home appliances	43,200/day	--	--	--
Television antennaes	--	--	--	--
Silverware	40,000/day	5	33	135
Instrument motors and electric clocks	112,000/day	--	--	--
Automobile manufacture	620,000/day	30	80	70
Unspecified		--	--	--
Metal fastener plant	89,000/day	52	302	--

[a]Analyses not shown are not available.

Table 9. Concentrations of Chromium in Body Tissues With and Without Known Exposures to Chromium (3)

Tissue	Reported Concentrations In Normal Tissues (ug/100g Wet Tissue)	Reported Concentrations In Chromate Worker Tissue (ug/100g Wet Tissue)
Lungs	0-33	130-9,887
Tracheobronchial lymph nodes	0-1	12-7,590
Kidney	0-9.6	0-211
Liver	1-11	0-159
Spleen	0-98	0-91
Abdominal lymph nodes	1	4-80
Stomach	0-5	4-11
Intestines	10	4-5
Muscle	0-8	0-19
Pancreas	21	8-36
Thyroid	43	24-53
Adrenal	0-41	5-76
Brain	0-4	0-5
Bone	5	0-292

Table 10. Experimental Animal Exposures to Chromate (3)

Species	Type of Exposure	Material	Avg. Dose of Concentration	Duration	Effect
Rats	Ingestion	K_2CrO_4 in drinking water	500 ppm	daily	maximum non-toxic level
Mature Rats & Mice	Ingestion	$ZnCrO_4$ in feed	1%	daily	maximum non-toxic level
Young Rats	Ingestion	$ZnCrO_4$ in feed	0.12%	daily	maximum non-toxic level
Young Rats	Ingestion	K_2CrO_4 in feed	0.12%	daily	maximum non-toxic level
Dogs	Ingestion	$K_2Cr_2O_7$ in feed	0.01-0.02 gm. as Cr	daily	fatal in 3 months
Dogs	Subcutaneous	$K_2Cr_2O_7$	210 mg. as Cr	-	rapidly fatal
Rabbits & Guinea Pigs	Subcutaneous or Intravenous	Na_2CrO_4	0.1-0.3 g as CrO_3	-	rapid death
Monkeys	Subcutaneous	$K_2Cr_2O_7$	0.02-0.07 g in a 2% solution	-	fatal

Table 11. Cancerous Responses at the Sites of Implantation of Chromium Compounds into Rats (12).

Compound	Route 35 Rats	No. Cancers at Site	Percent Cancer Yield	Latent Period (Min)
Chromic Chromate	1M	30	86	7
$Cr_2(CrO_4)_3$	1P1	34	97	7
Calcium Chromate	1M	10	29	7
$CaCrO_4$	1P1	28	80	7
Sodium Dichromate	1M	0	0	-
$Na_2Cr_2O_7$	1P1	1	3	10
Chromium Metal	1M	0	0	0
	1P1	0	0	0
Chromite Ore	1M	0	0	0
	1P1	0	0	0

Note: 1M - Intramuscular Implantation
1P1 - Intrapleural Implantation

Table 12. Lethal Concentrations of Chromium Ions for Fish (15)

Fish	Ion	Source	Concentration (ppm)	Survival Time (Hr)	Hours to Kill Half of the Fish
Rainbow Trout	Cr(VI)	K_2CrO_4	20	60	-
		K_2CrO_4	50	30	-
		K_2CrO_4	1000	1	-
		K_2CrO_4	30	-	48
		K_2CrO_4	20	70	-
		K_2CrO_4	100	-	24
Brown Trout	Cr(VI)	-	5.2	48	-
Largemouth Bass	Cr(VI)	K_2CrO_4	195	-	48
		K_2CrO_4	65	144	-
Goldfish	Cr(VI)	CrO_3	52	96	-
		$K_2Cr_2O_7$	176	72	-
Salmon (fresh H_2O)	Cr(VI)	-	10	-	-
(salt H_2O)		-	17.8	-	-
Bluegill	Cr(VI)	$K_2Cr_2O_7$	110	-	96
Sticklebacks	Cr(III)	$KCr(SO_4)_2$	2	48	-
Eels	Cr(III)	$KCr(SO_4)_2$	5.2	20	-

Table 13. Reaction Rates for Various Sulfur Dioxide: Cr(VI) Molar Ratios (27)

Solution pH	1.0	1.5	2.0	3.0	4.0	5.0
SO_2:Cr(VI)	1	1	1	1	1	1
Reaction Time (minutes)	0.5	1-1.5	5-6	5-6	18-22	60-90
SO_2:Cr(VI)	2	2	2	2	2	2
Reaction Time (minutes)	0.5	1-1.5	6-8	22-25	43-48	450-480
SO_2:Cr(VI)	3	3	3	3	3	3
Reaction Time (minutes)	0.5	2-2.5	9-12	30-35	60-70	infinite

Table 14. Ionization and Solubility Product Constants at 18-20°C (36-41)

Ionic Equation	Constant
$H_2CrO_4 = H^+ + HCrO_4^-$	K = 0.18
$HCrO_4^- = H^+ + CrO_4^{-2}$	K = 3.2 x 10^{-7}
$Cr_2O_7^{-2} + H_2O = 2HCrO_4^-$	K = 0.023
$\frac{1}{2}CrO_7^{-2} + \frac{1}{2}H_2O = HCrO_4^-$	K = 0.15
$\frac{1}{2}Cr_2O_7^{-2} + \frac{1}{2}H_2O = H^+ + CrO_4^{-2}$	K = 4.8 x 10^{-8}
$Cr(OH)_3 = Cr^{+3} + 3OH^-$	K_{sp} = 6 x 10^{-31}
$Cr(OH)_3 = CrO_2^- + H^+ + H_2O$	K_{sp} = 9 x 10^{-17}

Table 15. Stoichiometry of Waste Treatment Reactions (1,5,36,37,38)

No.	Chemical	(¢/lb.)	(lb/lb.Cr)	Reaction
1	SO_2	13.0	1.9	$SO_2 + H_2O = H_2SO_3$
				$2H_2CrO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + 5H_2O$
2	$Na_2S_2O_5$	5.3	2.8	$Na_2S_2O_5 + H_2O = 2NaHSO_3$
				$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O$
3	$NaHSO_3$	2.8	3.0	(same as 2)
4	Na_2SO_3	4.3	3.6	$3Na_2SO_3 + 3H_2SO_4 + 2H_2CrO_4 = Cr_2(SO_4)_3 + 3Na_2SO_4 + 5H_2O$
5	$FeSO_4$	1.2	8.8	$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2H_2O$
6	$BaCl_2$	7.1	4.0	$BaCl_2 + Na_2CrO_4 = BaCrO_4 + 2NaCl$
7	$Ca(OH)_2$	1.2	2.2	$Cr_2(SO_4)_3 + 3Ca(OH)_2 = 2Cr(OH)_3 + 3CaSO_4$
8	NaOH	4.9	2.4	$Cr_2(SO_4)_3 + 6NaOH = 2Cr(OH)_3 + 3Na_2SO_4$
9	Na_2CO_3	3.6	3.2	$Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Cr(OH)_3 + 3Na_2SO_4 + 3CO_2$

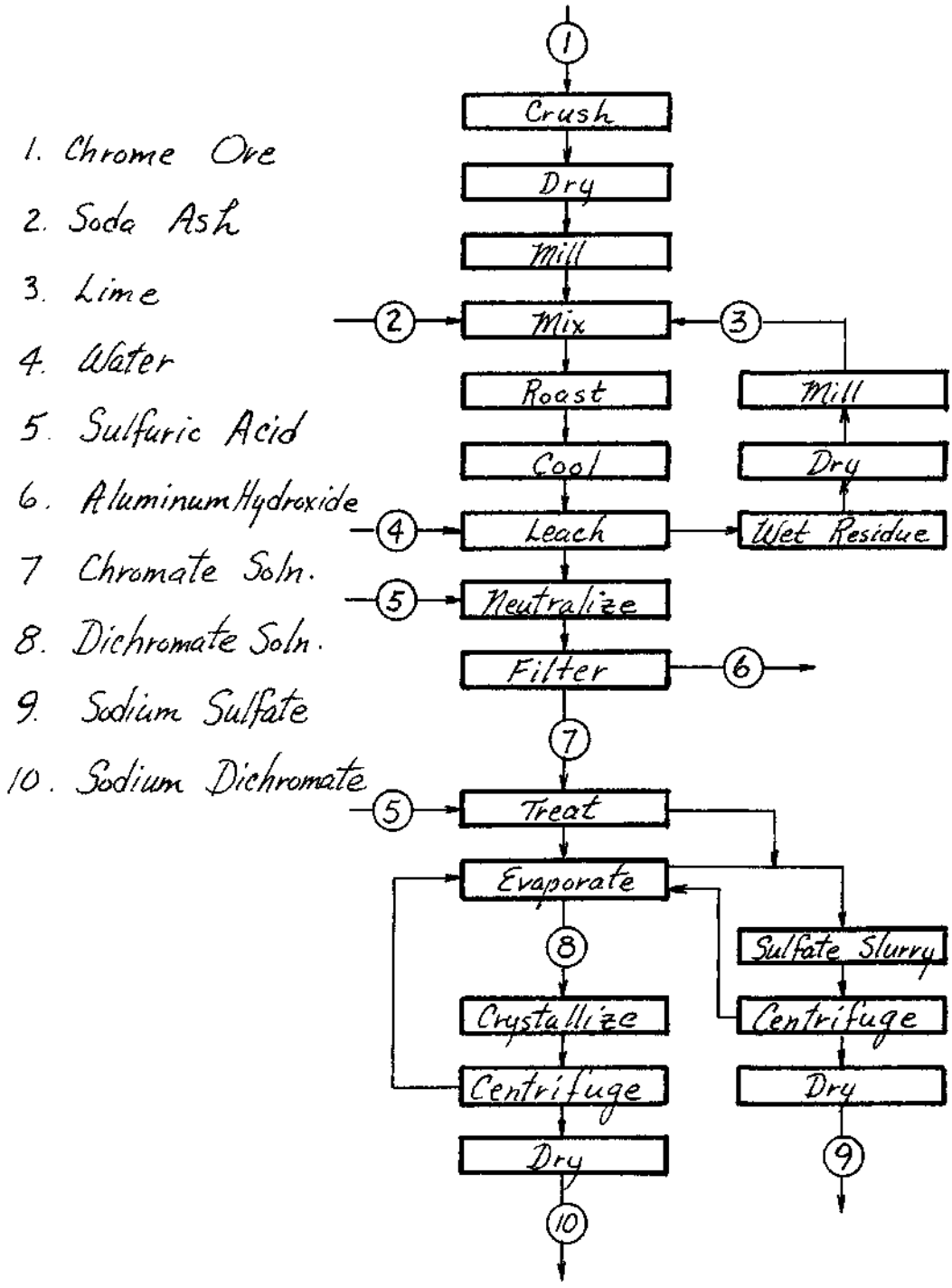

Figure 4. Flow Sheet For The Manufacture Of Sodium Dichromate(5)

Analytical Procedure for Total Chromium

1. Dilute 10 ml. of waste solution to 500 ml.

2. Pipet 5 ml. of diluted solution and add approximately 100 ml. of deionized water.

3. Add 2 gm. of sodium peroxide and dissolve.

4. Heat to boiling and boil until the excess peroxide is expelled (approximately 30 minutes).

5. Filter and wash the precipitate with sodium hydroxide solution (pH = 9).

6. Add concentrated sulfuric acid until neutral and then add 5 ml. excess.

7. Cool solution to ambient temperature.

8. Add 2 gm. of potassium iodine and titrate immediately with thiosulfate solution to a yellow color.

9. Add 5 ml. of 1 percent soluble starch solution.

10. Titrate until the blue color disappears.

11. Use equation 1 on page 44 to calculate the chromium concentration.

Analytical Procedure for Hexavalent Chromium

1. Dilute 10 ml. of waste solution to 500 ml.
2. Pipet 5 ml. of diluted solution and add approximately 100 ml. of deionized water.
3. Add ammonium hydroxide to a pH of 9.
4. Boil the solution for two minutes.
5. Filter and wash the precipitate with sodium hydroxide solution (pH = 9).
6. Add concentrated sulfuric acid until neutral and then add 5 ml. excess.
7. Cool solution to ambient temperature.
8. Add 2 gm. of potassium iodine and titrate immediately with thiosulfate solution to a yellow color.
9. Add 5 ml. of 1 percent soluble starch solution.
10. Titrate until the blue color disappears.
11. Use equation 1 on page 44 to calculate the hexavalent chromium concentration.

Analytical Procedure for Chromic Oxide Purity

1. Heat the sample at 250 F. for 1 hour.
2. Cool to ambient temperature in a desiccator.
3. Weigh out 0.02 to 0.2 grams of sample.
4. Mix with 5 grams of sodium peroxide.
5. Fuse the mixture in an iron or Ni crucible.
6. Cool and dissolve in deionized water.
7. Add 20 ml. of 30 percent hydrogen peroxide and boil until the excess peroxide is expelled (approximately 45 minutes).
8. Filter and wash the precipitate with sodium hydroxide solution (pH = 9).
9. Add Concentrated sulfuric acid until neutral and then add 5 ml. excess.
10. Cool solution to ambient temperature.
11. Add 2 gm. of potassium iodine and titrate immediately with thiosulfate solution to a yellow color.
12. Add 5 ml. of 1 percent soluble starch solution.
13. Titrate until the blue color disappears.
14. Use equation 3 on page 44 to calculate the chromic oxide purity.

Sample Calculations

1. For Hexavalent and Total Chromium

$$\frac{\text{mg.Cr}}{\text{liter}} = \frac{(1000)(17.332)}{(\text{ml. sample})} \cdot \frac{(\text{normality of titer})(\text{ml. of titer})}{(\text{sample dilution})}$$

2. For Trivalent Chromium

Cr(III) = Total Cr - Cr(VI)

3. For Chromic Oxide %

$$\%Cr_2O_3 = \frac{(\text{ml.Titer})(\text{normality of titer})}{(\text{wt. of sample})} \cdot \frac{(17.332)(151.9902)}{(103.992)} \cdot 100\%$$

(for example)

Sample #1 required 37 ml. of 0.1N $Na_2S_2O_3$ for 105.1 mg. of sample (after leaching)

$$\%Cr_2O_3 = 89.2\%$$

Sample #2 required 34.4 ml. of 0.1N $Na_2S_2O_3$ for 97.1 mg. of sample (after leaching)

$$\%Cr_2O_3 = 89.7\%$$

Sample #3 required 24.05 ml. of 0.1N $Na_2S_2O_3$ for 147.4 mg. of sample (after roasting)

$$\%Cr_2O_3 = 41.3\%$$

BIBLIOGRAPHY

1. Metal Finishing Guidebook Directory For 1971, 39th Annual Edition, Metals and Plastics Publications, Inc., Westwood, N. J., 1971

2. Chromium Monthly Mineral Industry Survey, U.S. Bureau of Mines, June 1971

3. Udy, M. J., Editor, Chromium, Vol. 1, Chemistry of Chromium and Its Compounds, American Chemical Society Monograph No. 132, Reinhold Publishing Corp., New York 1956

4. Udy, M. J., Editor, Chromium, Vol. 2, Metallurgy of Chromium and Its Alloys, American Chemical Society Monograph No. 132, Reinhold Publishing Corp., New York, 1956.

5. A State of the Art Review of Metal Finishing Waste Treatment, Federal Water Quality Administration, Water Pollution Control Research Series No. 12010 EE, November 1968

6. Steinmatz, C. E., "Blowdown Toxicity Banished in 90,000 GPD System" Chemical Processing, p. 17, September 1971

7. Kelly, Bernard J., "A Comparison of Ion Exchange and Reduction Processes for Removing Chromates from Cooling Tower Blowdown," Industrial Water Engineering, Volume 5, No. 9, p. 34, 1968

8. Activated Sludge Treatment of Chrome Tannery Wastes, Federal Water Quality Administration, Water Pollution Control Research Series No. 12120, September 1969

9. Mertz, W., "Biological Role of Chromium," Federation Proceedings, Vol. 26, p. 186, 1967

10. Samitz, M. H., Scheiner, D. M., and S. A. Katz, "Ascorbic Acid in the Prevention of Chrome Dermatitis," Archives of Environmental Health, Vol. 17, p. 44, 1968

11. Baetjer, A. M., and C. H. Steffee, "Histopathologic Effects of Chromate Chemicals," Archives of Environmental Health, Vol. 11, p. 66, 1965

12. Hueper, W. C. and W. W. Payne, "Experimental Studies in Metal Carcinogenesis," Archives of Environmental Health, Vol. 5, p. 445, 1962

13. Alton, D. W., "A Continuous Monitor for Hexavalent Chromium in River Water," Atomic Energy Commission Report BWNL-1168, October 1969

14. Pickering, Q. H., and C. Henderson, "The Acute Toxicity of Some Heavy Metals to Different Species of Warmwater Fishes," Air and Water Pollution, Vol. 10, p. 453, 1966

15. Benoit, R. J., and F. B. Trama, "Toxicity of Hexavalent Chromium to Bluegills," J. Water Pollution Control Federation, Volume 32, p. 868, 1960

16. Pollution Caused Fish Kills, Annual Report, Federal Water Pollution Control Administration, p. 5, 1968

17. Pollution Caused Fish Kills, Annual Report, Federal Water Pollution Control Administration, p. 7, 1969

18. Ingols, R. S., and R. H. Fetner,"A Study of the Toxicity of the Toxicity of Chromium in Sewage Treatment Processes," Project No. B-108 and B-113, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia, January 1958

19. Ingols, R. S., and R. H. Fetner, "Toxicity of Chromium Compounds Under Aerobic Conditions," J. Water Pollution Control Federation, Volume 33, p. 336, 1961

20. Stankey, S. A., "Effects of Chromium Wastes on Activated Sludge," Sewage and Industrial Wastes, Volume 31, p. 496, 1959

21. Tarwin, D., "Metal Plating Wastes and Sewage Treatment," Sewage and Industrial Wastes, Volume 28, p. 1371, 1956

22. Kanai, M., "Waterway Treatment by Electrolysis in the Presence of Calcium Fluoride," Proceedings of the 24th Industrial Waste Conference at Purdue University, Engineering Extension Series No. 135, 1969

23. Dvorin, R., "Dialysis for Solution Treatment in the Metal Finishing Industry," Metal Finishing, p. 52, April 1959

24. Serota, L., Ion Exchange Properties," Metal Finishing, Volume 56, p. 68, April 1958

25. Gray, A. G., "Recovery and Treatment of Plating Wastes," Products Finishing, Volume 17, P. 42, January 1953

26. Hodges, Milton E., "Treatment of Chromium and other Plating Room Wastes," Metal Finishing, Volume 51, p. 60, October 1953

27. Chamberlain, N. S. and R. V. Day, "Technology of Chrome Reduction with Sulfur Dioxide," Proceedings of the 11th Industrial Waste Conference at Purdue University, Engineering Extension Series No. 91, p. 129, 1956

28. "Plating Waste Treatment at Proctor-Silex," Products Finishing Volume 35, No. 4, p. 43, 1971

29. Serota, L., "Treatment of Chrome Wastes," Metal Finishing, Volume 55, p. 65, September 1957

30. Handbook of Chemistry and Physics, 35th Edition, 1953-54, p. 482, Chemical Rubber Publishing Co., Cleveland, Ohio

31. James, D. L. and R. R. Lee, Economics of Water Resources Planning, McGraw-Hill Book Co., 1971

32. Tables of Useful Lives of Depreciable Property, IRS Publication No. 173, U.S. Treasury Department, p. 11, 1960

33. Kunin, R. and D. G. Downing, "Ion Exchange System Boasts More Pulling Power," Chemical Engineering, p. 67, June 28, 1971

34. Oil, Paint and Drug Reporter, Schnell Publishing Co., New York, June 21, 1971

35. Kirk-Othmer Encyclopedia of Chemical Technology, Volume 15, 2nd Edition, Interscience Publishers, New York 1968

36. Day, R. V., "Disposal of Plating Room Wastes," Plating Volume 46, p. 929, August 1959

37. Ceresa, M., and L. E. Lancy, "Metal Finishing Waste Disposal Part III," Metal Finishing, Volume 66, p. 112, June 1968

38. Clifford, A. F., Inorganic Chemistry of Qualitative Analysis, Prentice-Hall, 1961

39. Lange, N. A., Handbook of Chemistry, 10th Edition, McGraw-Hill, 1961

40. McCarty, P. L. and C. N. Sawyer, Chemistry for Sanitary Engineers, 2nd Edition, McGraw-Hill, 1967

41. Pauling, L., General Chemistry, 2nd Edition, W. H.Freeman and Co. 1954